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A NEW METHODOLOGY FOR CHARACTERIZATION OF ENVIRONMENTALLY IMPORTANT RADIONUCLIDE SPECIES *VIA* SURFACE-ENHANCED RAMAN SCATTERING (SERS)

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INTRODUCTION

Selective and sensitive detection and characterization of radionuclide contaminants in subsurface environments is essential to safely and cost-effectively locate, treat, isolate or destroy contaminants encountered in DOE's environmental cleanup activity. Currently, techniques for monitoring and characterizing radionuclides include inductively coupled plasma mass spectrometry (ICP-MS), numerous optical methods, electrochemistry, chromatography and chemical analysis methods. Among these techniques, the optical methods such as liquid scintillation counting[1] and spectrofluorimetry[2] offer excellent sensitivity. However, these optical techniques usually require chemical handling, *e.g.*, the use of complexing media, scintillation cocktails and phosphoric acids, in order to enhance signals. Furthermore, only fluorescent radionuclides [UO_2^{2+}, Cm(III), Am(III)] can be detected by the fluorimetry. Many environmentally-important radionuclides such as plutonium, neptunium and technetium species have no strong fluorescence signals and therefore can not be characterized *via* fluorescence spectroscopy. The research presented serves to replace existing radionuclide-detection techniques through the development of a novel surface-enhanced Raman scattering (SERS) spectroscopy to selectively and sensitively monitor and characterize the chemical speciation of radionuclides at trace levels. The SERS technique permits both of these measurements to be made simultaneously and results

in significant improvement over current methods in reducing time of analysis, cost and sample manipulation.

RESULTS AND DISCUSSION

A new SERS substrate containing silver particles was prepared by an acid-catalyzed sol-gel method. Silver nitrate was first doped into the sol-gel film followed by chemical reduction of silver ions with sodium borohydride to produce silver particles. This substrate was found to be very active for the enhancement of the uranyl Raman signal. A SERS peak at 700-710 cm^{-1} (Fig.1) which is assigned to the O=U=O symmetric stretching vibration, was observed and the concentration of uranyl ions as low as 8.5×10^{-8} M was detected. Compared to the Raman band of uranyl ions in solution, which is located at 870 cm^{-1},[3] the lower frequency of the symmetric stretch indicates that there is a very strong interaction of uranyl ions with the silver surface. The detection limit obtained by this method is similar to that obtained with the UV-Vis spectrophotometric method and an order of magnitude higher than those of the ligand-modified silver colloid methods. Though the detection limit of our current SERS method based on the Ag-doped sol-gel films is higher than those of the fluorimetric and solution colloidal SERS methods, no preconcentration steps and complexing media are required in the present SERS method. The fluorescent band of uranyl ions is very broad, which can be interfered by the fluorescent signals from many potential organic species in environments. These organic species (*e.g.* humic acid) can also quench the fluorescent signals of uranyl ions, leading to diminished sensitivities of the fluorescent technique. The SERS detection of uranyl ions based on the sol-gel substrates could significantly overcome these problems. Furthermore, the improved stability of the silver particles in the sol-gel matrix compared to silver colloids enhances the potential application of these films to the quantitative detection and characterization of radionuclides in high-level nuclear waste products.

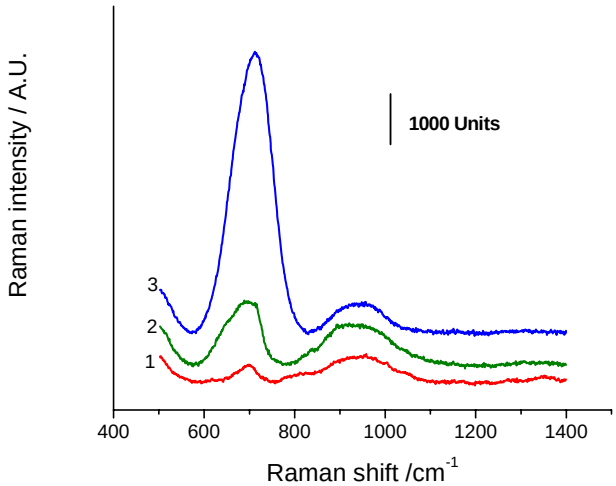

Figure 1. SERS spectra of uranyl ions adsorbed onto the silver-doped sol-gel substrate. 1: 8.5×10^{-8}, 2: 8.5×10^{-7}, 3: 8.5×10^{-6} M.

An additional comparison was made between the silver-doped sol-gel substrate and a film of silver-coated silica beads prepared by vacuum deposition of silver onto the beads. We found that the detection limit of the sol-gel substrate for uranyl ions was four orders of magnitude lower than that of the vacuum deposited substrate. Finally, the sol-gel SERS substrate was used to measure the surface-enhanced Raman signal of neptunyl ions, whose symmetric stretching vibration appeared at approximately 680 cm^{-1}. Although some work has been done to characterize neptunyl ions by normal Raman spectroscopy, to our knowledge, this is the first observation of a surface-enhanced Raman spectrum of neptunyl ions.

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